

FORMATION OF STABLE ELECTRONIC CONFIGURATIONS OF SOME PHYSICAL PROPERTIES
OF TRANSITION METAL CARBIDES AND NITRIDES IN THE RANGE OF THEIR HOMOGENEITY

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FORMATION OF STABLE ELECTRONIC CONFIGURATIONS OF SOME PHYSICAL PROPERTIES OF TRANSITION METAL CARBIDES AND NITRIDES IN THE RANGE OF THEIR HOMOGENEITY

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ABSTRACT: Data on resistance change, thermoelectromotive force, superconductivity of the monocarbides of Ti, Zr, Hf, Nb, and Ta, and on the mononitrides of Ti, Zr, Nb, and Ta in the area of homogeneity were studied.

It is known [1-8] that the physical properties of carbides and of transition metal nitrides, such as specific electric resistance, the transition point of the state of superconductivity, the thermoelectromotive force coefficient, thermal conductivity, and other properties, change as a function of the content of nonmetal in the region of the homogeneous phase, e.g., carbides depending on the degree of completion of the carbon sublattice.

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We may assume that the degree of completion of the metal lattice by atoms of nonmetals causes the deterioration of stable electronic configurations and the probability of the appearance of statistical density in stable configurations. This depends on both the structure of the metal atom and the structure of the nonmetal atom in the segregated state, and also on the relative concentration of configurations of various types.

In relation to the specific electrical resistance of transition metals, we may conclude that the specific electrical resistance of all carbides decreases in the region of homogeneity if their phase composition approaches stoichiometric proportions (in relation to carbon content).

Thus, for example, the specific electrical resistance of TiC decreases with the increase of carbon concentration in phase [5], which can be explained by the formation of stable electronic sp^3 configurations of carbon, while for titanium, which has the configuration of outside electrons d^2s^2 , the donation of these electrons is most probable at the formation of the d^0 -state. The donated electrons are partly used for stabilization of the sp^3 configurations, and these electrons become, in part, conductivity electrons. With the decrease of carbon content in titanium carbide, the possibility of transition of electrons from titanium atoms to carbon atoms decreases, and therefore the concentration of collective electrons increases, along with the electrical resistance.

A similar dependence of specific electrical resistance upon the content of bonded carbon exists for the carbides of zirconium [1] and hafnium** (Fig. 1,a), since all three metals have a monotypic configuration of outer electrons - d^2s^2 . Because of the simultaneous increase of the energetic stability of the d-state (with preference for the most stable d^5 -state) and the increase of the principal quantum numbers of d-electrons, upon the transition from Ti to Hf, the statistical density of the d^5 -state increases and the number of electrons,

*Numbers in margin indicate pagination in foreign text.

**The specific electrical resistance of HfC in the area of homogeneity has been measured by the authors of the present paper.

transferable from the metal, decreases. This results, first, in the decrease of the specific electrical resistance, and second, in the increase of the melting point of the corresponding carbide phases, because less loosening of the lattice occurs.

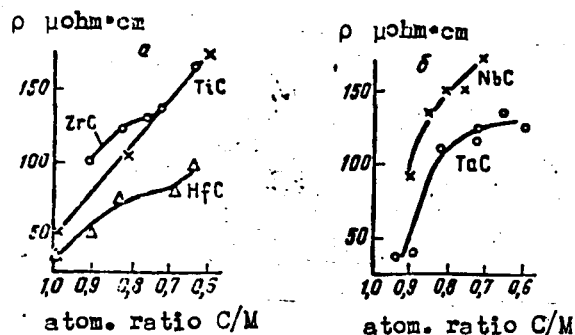


Fig. 1. Dependence of the Specific Electrical Resistance of TiC, ZrC, HfC (a) and NbC, TaC (b) on Carbon Content in the Homogeneity Area

Another type of dependence of specific electrical resistance has been observed for the carbides of niobium and tantalum [1,2]. Here, the specific electrical resistance initially decreases relatively slowly, with the increasing concentration of bonded carbon, and then sharply decreases upon approaching stoichiometric composition (Fig. 1,b). Considering the fact that the segregated Nb atom has the electronic configuration d^4s^1 and Ta - d^3s^2 , which are closer (particularly in the case of Nb) to the stable state d^5 , the dependence of the specific electric resistance observed on the bonded carbon concentration can be explained by the following condition, opposing that existing for carbides TiC and ZrC. In addition to the stable sp^3 configuration

of carbon, the electronic configurations of the atoms of the metal sublattice are closer to the stable state d^5 , causing lower availability of their electrons for conductivity and, simultaneously, a decrease in the dispersion of conductivity /1971 electrons.

The nitrogen atoms in transition metal compounds, of which the number of electrons on the d-shell n_d is approximately 5, tend to form a stable configuration by donating one p-electron by the mechanism $s^2p^3 \rightarrow s^2p^2 + p \rightarrow sp^3 + p$. This split off electron transfers either into the common collective of conductivity electrons, or is used for completion of the d-level of the metal. In the case of nitrogen compounds of transition metals, however, where n_d is not high and where donor capacity is primarily developed, we must expect the capture of metal electrons by nitrogen atoms when stable configurations s^2p^6 are formed. The latter mechanism corresponds to experimental data on the electroconductivity of the nitrides TiN and ZrN [4] (Fig. 2,a). Atoms of the metals Ti and Zr, having a small value of n_d , are primarily responsible for the development of donor capacity, and their donated electrons are basically employed for the formation of stable configurations of s^2p^6 type nitrogen atoms which complete their outer shell. Stable d^0 -states of metal atoms are formed by this mechanism. As a result, the dispersing capacity of atoms in the nitride lattice is lowered, causing a sharp decrease in the specific electrical resistance of the phase when saturated with nitrogen.

Nb and Ta atoms have a large n_d value and are less inclined toward d-electron donation than Ti and Zr electrons (particularly the Nb atoms). Thus, in the nitrides NbN and TaN, stable configurations of the sp^3 type should be formed with the donation of an electron used for completion of the outer d-shell /1972

of metal atoms. In this mechanism, the niobium atoms in the separate state have the configuration of outer electrons d^4s^1 and they require less electrons for the formation of the stable d^5 -state than the tantalum atoms. Therefore the specific electrical resistance of NbN is lower than that of TaN (for phases of saturated composition in the region of homogeneity), due to the enrichment of the conductivity electron collective at the expense of p-electrons of nitrogen [6] (Fig. 2,b).

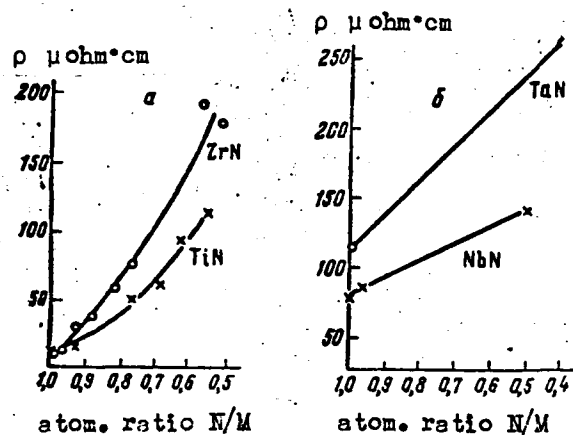


Fig. 2. Dependence of the Specific Electrical Resistance of TiN, ZrN (a), and NbC, TaC (b) on the Nitrogen Content in the Homogeneity Area

The Ta and Nb carbides are superconductive. The transition temperature leading into the superconductive state depends on the bonded carbon content of the compound. This is obviously due to the fact that carbon atoms, having the stable configuration sp^3 in the compound, favor low dispersion of conductivity electrons, and the atoms Ta and Nb have the structure of outer electron shells d^3s^2 and d^4s^1 , respectively, close to the stable d^5 -state. Thus, as the carbon content approaches stoichiometric proportions in this phase, optimum conditions exist for the unhindered transport of conductivity electrons at appropriate low temperatures. Fig. 3 [7] shows the T_K dependence on carbon content in the phase, and it is also shown that NbC has a higher transition temperature than TaC, which can be explained by the structure of the outer d-shells of metal atoms, the latter being closer to the stable d^5 -state for Nb than for Ta.

Superconductivity also exists for the carbide Mo_2C , whose metal atom has the outer electron shell d^5s^1 in the free state, but its T_K , according to [9], has the value 2.78 K, whereas T_K for NbC and TaC are 11.1 and 9.7 K, respectively. It is significant that T_K of MoC is 9.26 K. Upon the formation of the carbide MoC from metal atoms, the electrons of the outer d-shell are partially used for the formation of M-C bonds. In the carbide Mo_2C , the amount of electrons donated by the d-shell of the metal atom for bonding is higher than in the carbide MoC. This explains the lower value of T_K for Mo_2C , since the decrease in the statistical density of stable d^5 -states in the crystal produces less favorable conditions for the transport of conductivity electrons without detectable dispersion. Such conditions are obtained only at lower temperatures, where superconductivity appears.

Superconductivity was not observed for the carbides of Ti, Zr, and Hf at temperatures as low as 1.20 K, which can be explained by the very small probability of a formation of stable d^5 -states, and by the fact that the formation of stable configurations d^0 , with the simultaneous appearance of a large number of collective conductivity electrons, cannot generate superconductivity because of the antibonding activity of the electrons.

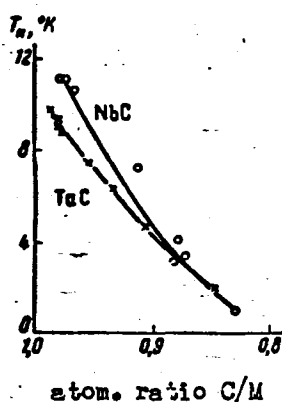


Fig. 3. Dependence of T_K of the Carbides TaC and NbC on Carbon Content in the Homogeneity Area [7]

Most transition metal nitrides also show superconductivity with a T_K of various values, depending on the electronic structure of metal and nonmetal. Thus for the transition metal nitrides of group IV - TiN, ZrN, and HfN - the T_K values are 5.6, 10.7, and 6.2, respectively, [9] for phases of saturated composition. Since the n_d value is very small for the atoms of these metals, upon the formation of their compounds with nitrogen, the d-electrons are primarily used to form stable configurations of the s^2p^6 type with nitrogen atoms. On the other hand, the metal atoms themselves attempt the formation of stable d^0 -states, where energetic stability increases from Ti to Zr and further to Hf, with the increase of the principal quantum number of d-electrons, as shown by the increase of T_K from TiN to ZrN. Hafnium nitride, however,

has a lower T_K than ZrN, possibly because of the high energetic stability of the d-level of Hf atoms, which impedes the donation of electrons for stabilizing the configuration of nitrogen atoms. Thus the probability of conditions for the appearance of superconductivity decreases and shifts in direction to lower temperatures.

The atoms of the elements of group V, - V, Nb, and Ta have higher n_d values. /1973 Therefore there is a greater tendency to capture electrons which attempt to establish stable d^5 -states, and the stability of d^5 -states increases with the principal quantum number. When compounds of these elements are formed with nitrogen, they may receive electrons from the nitrogen atoms which donate one electron upon formation of the stable sp^3 configuration. Particularly favorable conditions for this mechanism exist with NbN, which has the highest T_K values of all the compounds discussed. The Mo nitride seems to provide even better conditions for the appearance of superconductivity, since the molybdenum atom has the outer electron shell structure d^5s^1 . However, when the Mo nitride compound is formed with nitrogen, electrons appear which are generated upon the establishment of the sp^3 nitrogen configuration, which contribute to the collective of conductivity electrons, and which have an adverse effect on superconductivity.

Fig. 4 [8] shows the dependence of T_K on the content of bonded nitrogen. The graph indicates that the decrease of T_K is more acute for ZrN than for NbN. As shown before, stable configurations s^2p^6 appear when ZrN is formed, and the metal atoms attempt to form the d^0 -state. When the content of bonded nitrogen in the phase decreases, the statistical density of d-states should decline, since the smaller amount of nitrogen atoms require less electrons for the formation of s^2p^6 configurations. These electrons are supplied by the d-shells of metal atoms, thus causing a sharp decrease of T_K . For the nitride NbN, whose metal atoms attempt the formation of stable d^5 -states, the number of electrons required for this process is small and the demand is readily satisfied by a smaller amount of bonded nitrogen. In addition, a much smaller change of the T_K value is observed when the amount of bonded nitrogen decreases.

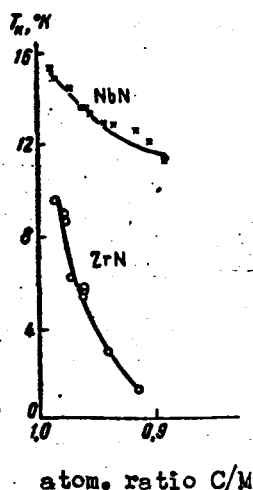


Fig. 4. Dependence of T_K of the Nitrides ZrN and NbN on the Nitrogen Content in the Homogeneity Area [8]

The magnitude of the coefficient of the thermoelectromotive force increases with the content of bonded nitrogen in the phase [1], while the coefficient of the thermoelectromotive force increases more sharply for ZrC than for NbC. This can be tentatively explained by the donation of d-electrons by Zr atoms, which attempt formation of stable d^0 -configurations. The atoms of Nb, on the other hand, are more inclined to capture electrons for formation of stable d^0 -states, causing a smaller increase in the concentration of conductive electrons, and subsequently, a smaller thermoelectromotive force coefficient. Titanium carbide also has a relatively high coefficient of thermoelectromotive force [5], since Ti atoms attempt to form stable d^0 -configurations, supplying the collective of conductivity electrons. /1974

For the nitrides of Ti and Zr, the value of the coefficient of thermoelectromotive force increases also with the content of bonded nitrogen [4], but the values of these coefficients for the nitride phases of saturated composition (particularly for TiN and TiC) differ from the values for the carbide phases. Since Ti and Zr atoms contribute to the completion of the s^2p^6 configuration of nitrogen when the formation of nitrides ($d + s$) - electrons occurs, the concentration of free electrons decreases, and consequently the values of the coefficient of thermoelectromotive force.

With the nitrides of Nb and Ta, the coefficients of thermoelectromotive force decrease with the increase of the bonded nitrogen content [6]. The outer shells of Nb and Ta atoms have, as indicated before, the tendency to capture electrons, and the number of captured electrons are higher for Ta than for Nb. This results in the decrease of the concentration of conductivity electrons, and consequently in lower values of the coefficient of thermoelectromotive force.

Some studies on the thermal conductivity of carbides and nitrides of transition metals [1,3] show an increase of the thermal conductivity coefficient of Zr and Nb carbides with the content of bonded carbon. Considering the conditions indicated before, the phenomenon can be explained by the increase of the electronic component of thermal conductivity, due to the increase in the concentration of free electrons. Thermal conductivity decreases for Nb and Ta nitrides with the increase of the content of bonded nitrogen, because of the decrease of the electronic component of thermal conductivity.

CONCLUSIONS

Data on resistance change, thermoelectromotive force, superconductivity of the monocarbides of Ti, Zr, Hf, Nb, and Ta, and on the mononitrides of Ti, Zr, Nb, and Ta in the area of homogeneity were studied, in respect to theories of

formation and deterioration of stable electronic configurations of the atoms of components.

It has been shown that with the decrease of the content of nonmetal (carbon, nitrogen) in the carbon or nitride homogeneity area, the statistical density of d^5 -configurations in the sublattice of the metal increases, causing a corresponding change in electrophysical properties. The metals of group IV and V show an essential difference in behavior, since the former represent primarily donors and the latter represent primarily acceptors of electrons.

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